

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



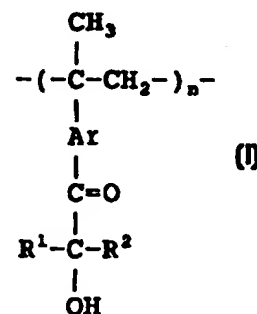
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 2/50, G03F 7/031		A1	(11) International Publication Number: WO 98/01479
			(43) International Publication Date: 15 January 1998 (15.01.98)
(21) International Application Number: PCT/NL97/00387		(81) Designated States: AU, CA, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 7 July 1997 (07.07.97)			
(30) Priority Data: 8/177800 8 July 1996 (08.07.96) JP		Published With international search report.	
(71) Applicants (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). JAPAN SYNTHETIC RUBBER CO., LTD. [JP/JP]; JSR Building, 2-11-24, Tsukiji, Chuo-ku, Tokyo 104 (JP). JAPAN FINE COATINGS CO., LTD. [JP/JP]; 2-11-24, Tsukiji, Chuo-ku, Tokyo 104 (JP).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): UKON, Masakatsu [JP/JP]; 2-15-2-401, Umezono, Tsukuba, Ibaraki 305 (JP). KATO, Keiko [JP/JP]; 1-13-33, Shirako Wako-City, Saitama-Prefecture 351-01 (JP). TAKAHASHI, Toshihiko [JP/JP]; 2-13-28-306, Kawaguchi, Tsuchiura, Ibaraki 300 (JP).			
(74) Agent: DEN HARTOG, Jeroen, Hendrikus, Joseph; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).			

(54) Title: RADIATION CURABLE RESIN COMPOSITION FOR MOLDING BY POLYMERIZATION IN DIES

(57) Abstract

A radiation curable composition for molding by polymerization in dies comprising, (A) a compound having at least one (meth)acrylate group and (B) a photopolymerization initiator being an oligomer having a molecular weight of about 300 to about 9000 and comprising on average more than 1.5 (α -ketone, β -hydroxydialkylethylbenzyl groups). Composition wherein the photoinitiator has a group represented by formula (I), wherein R^1 and R^2 are alkyl groups having 1 to 5 carbon atoms and n is a number of 2 to 50. The composition exhibits a high curing rate and produces molded products with a high transparency, excellent resistance to coloration upon exposure to light, and superior dimensional precision.



P14

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE OF THE INVENTION

5 RADIATION CURABLE RESIN COMPOSITION FOR MOLDING BY
 POLYMERIZATION IN DIES

BACKGROUND OF THE INVENTION

10

Field of the Invention

 The present invention relates to a radiation curable composition for molding by polymerization in dies which is rapidly cured by irradiating with actinic radiation such as ultraviolet rays, and, more particularly, to a radiation curable resin composition suitable for the manufacture of optical parts molded by polymerization in dies, such as lenses, optical disks, prisms, and lens sheets.

20

Description of Related Art

 Manufacturing plastic lens and the like by irradiating a radiation curable resin with ultraviolet rays from a mercury lamp as a source of actinic radiation has been proposed (Japanese Patent Applications Laid-open No. 194401/1986 and No. 207632/1988).

 According to this method, though there is an advantage that resins are cured in a short time by irradiation of ultraviolet rays, transparency of resulting lenses is inferior in comparison with those obtained from polymers such as polymethyl methacrylate, polycarbonate, or diethylene glycol bisarylcarbonate. Moreover, coloration due to exposure to light is a problem with the products cured by ultraviolet rays. In addition, when conventional radiation curable resins are molded by polymerization in dies, uncured compositions and unreacted components tend to be left inside the molded product so

that the molded product may warp or shrink due to volatilization or bleeding after the product has been removed from the die, impairing the dimensional accuracy of the product.

5 The present invention has been completed in view of these drawbacks in conventional photocurable resin compositions and has an object of providing a radiation curable resin composition suitable for molding by polymerization in dies at a high curing rate, producing
10 molded products with high transparency, exhibiting only small coloration due to exposure to lights, and possessing excellent dimensional precision.

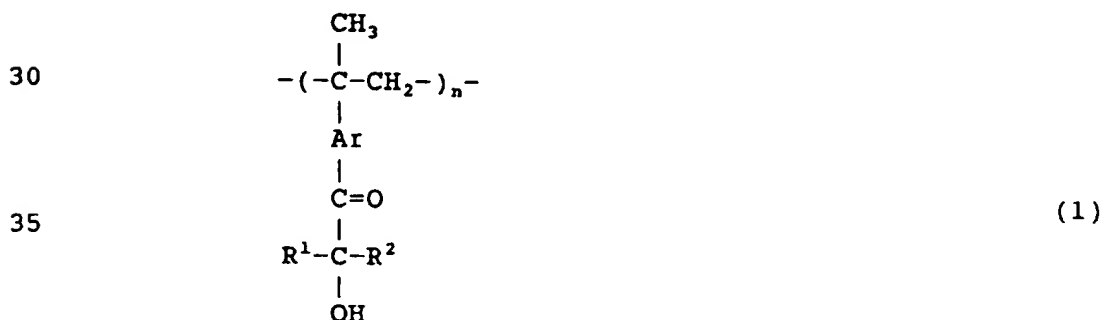
SUMMARY OF THE INVENTION

15 The above object of the present invention is achieved in the present invention by the provision of a radiation curable composition for molding by polymerization in dies comprising,

(A) a compound having at least one (meth)acrylate group
20 and

(B) a photopolymerization initiator being an oligomer having a molecular weight of 300-9000 and comprising on average more than 1.5 (α -ketone, β -hydroxyldialkyl-ethylbenzyl groups.

25 Preferably, the initiator comprises a group represented by the following formula (1),



wherein R^1 and R^2 are alkyl groups having 1 to 5 carbon atoms and n is a recurring number of the group (1).

5 DETAILED DESCRIPTION OF THE INVENTION
 AND PREFERRED EMBODIMENTS

Component (A) is at least one compound having at least one (meth)acrylate group. This compound, herein after also referred to as compound (A) may be either (1) a
10 polymer (including an oligomer) or (2) a monomer. Either one polymer or monomer or two or more of them may be used as the component (A).

The following compounds can be given as examples of the polymer having at least one(meth)acrylate group.
15 (i) A urethane (meth)acrylate which is obtained by a urethanization reaction of (a) a polyol having two or more hydroxyl groups in a molecule, (b) a polyisocyanate, and (c) a hydroxyl group-containing (meth)acrylate; (ii) an epoxy (meth)acrylate which is obtained by an epoxy
20 ring-opening reaction of (d) an epoxy compound and (e) (meth)acrylic acid; (iii) a polyester (meth)acrylate which is the reaction product of a polyester which is obtained from (a) a polyol and (f) a polybasic acid, and (e) (meth)acrylic acid; and (iv) other compounds such as a
25 polyamide (meth)acrylate, a siloxane possessing a (meth)acrylateoxy group, and the like. These compounds may be used individually or in combination of two or more.

Polyether polyols, polyester polyols, polycarbonate polyols, polycaprolactone polyols, and the
30 like are included in the polyol (a) which is used here. Two or more of these polyols may be used in combination. There is no specific limitation to the polymerization style of the structural unit in these polyols. The polymerization style may be either random polymerization,
35 block polymerization, or graft polymerization.

Examples of the above-mentioned polyether polyols, include aliphatic polyether polyols, alicyclic polyether polyols, and aromatic polyether polyols.

Examples of the aliphatic polyether polyols
5 include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether diols obtained by the ring-opening
10 copolymerization of two or more kinds of ion-polymerizable cyclic compounds.

Included in the examples of the ion-polymerizable cyclic compounds used here are cyclic ethers, such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide,
15 3,3-bischloromethyloxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, epichlorohydrin, glycidyl methacrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide,
20 vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, and butyl glycidyl ether.

Given as specific combinations of two or more ion-polymerizable cyclic compounds are the combinations of tetrahydrofuran and propylene oxide, tetrahydrofuran and
25 2-methyl tetrahydrofuran, tetrahydrofuran and 3-methyl tetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, butene-1-oxide and ethylene oxide, tetrahydrofuran/butene-1-oxide/ethylene oxide, and the like.

30 Further, a polyether diol obtained by the ring-opening copolymerization of the above-mentioned ion-polymerizable cyclic compound and a cyclic imine such as ethylene imine, a cyclic lactone acid such as β -propylactone or glycolic acid lactide, or a
35 dimethylcylopolysiloxane, can be used.

These aliphatic polyether polyols are commercially available under the trademarks of, for example, PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Co., Ltd.), PPG1000, EXCENOL 2020, EXCENOL 1020
5 (manufactured by Asahi Oline Co., Ltd.), PEG1000, Unisafe DC1100, Unisafe DC1800 (manufactured by Nippon Oil and Fats Co., Ltd.), PPTG2000, PPTG1000, PTG400, PTGL2000 (manufactured by Hodogaya Chemical Co., Ltd.), and
10 Z-3001-4, Z-3001-5, PBG2000A, PBG2000B (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.).

Examples of the alicyclic polyether polyols include alkylene oxide addition diol of hydrogenated bisphenol A, alkylene oxide addition diol of hydrogenated bisphenol F, alkylene oxide addition diol of
15 1,4-cyclohexane diol, and the like.

Examples of the aromatic polyether polyols, include alkylene oxide addition diol of bisphenol A, alkylene oxide addition diol of bisphenol F, alkylene oxide addition diol of hydroquinone, alkylene oxide
20 addition diol of naphthohydroquinone, and alkylene oxide addition diol of anthrahydroquinone. These aromatic polyether diols are commercially available under the trademarks, for example, of Uniol DA400, DA700, DA1000, and DA4000 (manufactured by Nippon Oil and Fats Co.,
25 Ltd.).

Examples of the polyester polyol, include polyester polyols obtained by the reaction of a polyhydric alcohol and a polybasic acid. Here, given as examples of the polyhydric alcohol are ethylene glycol, polyethylene
30 glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 3-methyl-1,5-pentane diol, 1,9-nonane diol, and 2-methyl-1,8-octane diol. As examples
35 of the polybasic acids, phthalic acid, isophthalic acid,

terephthalic acid, maleic acid, fumaric acid, adipic acid, and sebasic acid, are given. These polyester polyols are commercially available under the trademarks of Kurapole P-2010, PM1PA, PKA-A, PKA-A2, and PNA-2000 (manufactured by Kuraray Co., Ltd.).

Examples of the polycarbonate polyols include polycarbonate of polytetrahydrofuran, polycarbonate of 1,6-hexanediol, and commercially available products, such as DN-980, 981, 982, 983 (manufactured by Nippon Polyurethane Industries, Ltd.), PC-8000 (manufactured by PPG of the US), and PC-THF-CD (manufactured by BASF).

Further, examples of the polycaprolactone polyol include polycaprolactone diols obtained by the reaction of ϵ -caprolactone and a diol. Here, included in the examples of the diol are ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 1,4-butane diol, and the like. These polycaprolactone polyols are commercially available under the trademarks, for example, of PLACCEL 205, 205AL, 212, 212AL, 220, and 220AL (manufactured by Daicell Co., Ltd.).

Examples of polyols other than the above-mentioned polyols include ethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, hydrogenated bisphenol A, hydrogenated bisphenol F, dimethylol compounds of dicyclopentadiene, tricyclodecanedimethanol, pentacyclopentadecanedimethanol, β -methyl- δ -valerolactone, hydroxy terminal polybutadiene, hydroxy terminal hydrogenated polybutadiene, castor oil denatured polyol, polydimethylcyclohexane with terminal diols, polydimethylsiloxane carbitol denatured polyol, trimethylolpropane, pentaerythritol, ethylene oxide

addition triol of trimethylolpropane, ethylene oxide addition tetraol of pentaerythritol, and the like.

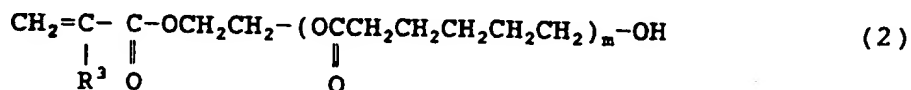
Among these polyols, ethylene oxide addition diol of bisphenol A, polytetramethylene glycol, and
5 polycarbonate of 1,6-hexanediol are particularly preferred.

The molecular weight of these polyols, in terms of number average molecular weight, is preferably in the range of 50 to 15,000, and particularly preferably 100 to
10 8,000.

Examples of the above-mentioned polyisocyanate (b) include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene
15 diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, aromatic ring hydrogenated
20 diisocyanate of these, 1,6-hexane diisocyanate, isophorone diisocyanate, methylene bis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, 1,4-hexamethylene diisocyanate, tetramethyl-xylylene diisocyanate (TMXDI), bis(2-isocyanatethyl)fumarate,
25 6-isopropyl-1,3-phenyl diisocyanate, 4,4'-diphenylpropane diisocyanate, lysine diisocyanate, and the like. These polyisocyanates may be used either individually or in combination of two or more.

Examples of the above-mentioned hydroxyl
30 group-containing (meth)acrylate (c) include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butane diol mono(meth)acrylate, 2-hydroxyalkyl (meth)acrylate phosphates, 4-hydroxy
35 cyclohexyl (meth)acrylate, 1,6-hexanediol

mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythrythol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, and (meth)acrylates
 5 represented by the following formula (2),



10

(wherein R^3 is a hydrogen atom or a methyl group, and m is a number of 1 to 15, preferably 1 to 4), and the compounds obtained by the addition reaction of a glycidyl group-containing compound, such as alkyl glycidyl ether,
 15 allyl glycidyl ether, or glycidyl (meth)acrylate, and (meth)acrylic acid. Of these, 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate are especially preferred.

Examples of the epoxy compound (d) include epoxy
 20 compounds such as bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, phenol novolak glycidyl ether, cresol novolak glycidyl ether, and glycidyl esters of aliphatic polybasic carboxylic acid, as well as dimers, trimers, tetramers, and pentamers of these epoxy compounds.

25 Examples of the polybasic acid (f) include phthalic acid, adipic acid, maleic acid, trimellitic acid, itaconic acid, succinic acid, and terephthalic acid.

It is desirable that the number average molecular weight of the polymer having at least one
 30 (meth)acrylate group used in the present invention is in the range of 300 to 20,000, and preferably 500 to 10,000.

The monomers having at least one (meth)acrylate group in a molecule include mono-functional compounds and poly-functional compounds. These monomers are reactive
 35 diluents used to tailor a variety of properties, and to

lower the viscosity of the polymer. Both mono- and poly-functional compounds can be used in the present invention. The mono-functional compounds are mainly used when a cured product with a relatively low modulus of elasticity is
5 desired. The modulus of elasticity of the cured product can be controlled by jointly using poly-functional and mono-functional compounds at an appropriate ratio.

An example of a desirable mono-functional compound is a bisphenyl compound, comprising one
10 (meth)acrylate group and comprising two aromatic rings, wherein the (meth)acrylate group is bound to an aromatic ring through at least one alkoxy group, wherein the alkoxy group may be an alkylene group or a hydroxyl alkylene group having 2 to 6 carbon atoms, and the compound may
15 comprise 1-12 alkoxy groups, and wherein the two aromatic groups may be phenyl groups bound to each other directly, or by a bridging organic group.

Examples of the alkylene group or the hydroxyl alkylene group containing 2 to 6 carbon atoms are: 1,2-
20 ethyl, 1,3-propyl, 1,2-propyl, 1,4-butyl, 1,2-butyl, 1,4-pentyl, 1,4-(2-methyl)-butyl, 1,5-pentyl and 2-hydroxy-1,3-propyl.

In particular, 1,2-ethyl, 1,2-propyl, 1,4-butyl, 1,2-butyl, 1,4-(2-methyl)-butyl or 2-hydroxy-
25 1,3-propyl are preferred.

Preferably, the number of alkoxy groups is in the range of 1-5, and more preferably 1-3.

In case the two phenyl groups are bound to each other via a bridging group, this bridging group preferably
30 is a 2,2'-propyl, 2,2'-hexafluoropropyl, methyl or sulphonyl group. Of these, 2,2'-propyl is particularly preferred.

Examples of this compound include the (meth)acrylic acid ester of ethylene oxide addition
35 p-cumylphenol, (meth)acrylic acid ester of propylene oxide

addition p-cumylphenol, and the like. These compounds can be obtained by the addition reaction of ethylene oxide or propylene oxide to p-cumylphenol, followed by the reaction with (meth)acrylic acid. Among these compounds,

- 5 (meth)acrylic acid ester of ethylene oxide addition p-cumylphenol is especially desirable, and Aronix M110 (manufactured by Toagosei Chemical Industry Co., Ltd.) can be given as a commercially available product.

- Further, specific examples of this compound
10 include 2-hydroxy-3-(o-phenylphenoxy)propyl acrylate, 2-(o-phenylphenoxy)ethyl acrylate, 2-[2-(o-phenylphenoxy)ethoxy]ethyl acrylate, and the like. These compounds can be obtained by the addition reaction of an alkylene oxide and phenyl phenol, followed by the
15 reaction with (meth)acrylic acid. TO-1317 (manufactured by Toagosei Chemical Industry Co., Ltd.) can be given as an example of commercially available products.

- The following compounds are given as examples of mono-functional compounds other than those mentioned
20 above: 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl
25 (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, iso-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl
30 (meth)acrylate, iso-decyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, octadecyl (meth)acrylate, stearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol
35 (meth)acrylate, benzyl (meth)acrylate, cyclohexyl

(meth)acrylate, phenoxyethyl (meth)acrylate, phenoxy polyethylene glycol (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxy ethylene glycol

5 (meth)acrylate, ethoxyethyl (meth)acrylate, methoxy polyethylene glycol (meth)acrylate, methoxy polypropylene glycol (meth)acrylate, dicyclopentadienyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, tricyclodecanyl (meth)acrylate,

10 (meth)acryloyl morpholine, isobornyl (meth)acrylate, bornyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, 2-(meth)acrylateoxyethyl phthalic acid, 2-(meth)acrylate oxyethylhexahydro phthalic acid, 2-(meth)acrylateoxypropyl

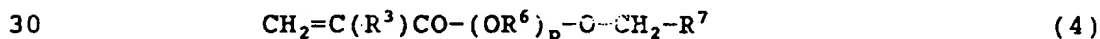
15 phthalic acid, 2-(meth)acrylateoxypropyltetrahydro phthalic acid, 2-(meth)acrylateoxypropylhexahydro phthalic acid, 2-(meth)acrylateoxyethyl succinic acid, and the compounds represented by the following formulas (3) to

20 (6).



wherein R^3 is a hydrogen atom or a methyl group, R^4 is an

25 alkylene group having 2 to 6, preferably 2 to 4, carbon atoms, R^5 is a hydrogen atom or an alkyl group having 1 to 12, preferably 1 to 9, carbon atoms, and m is an integer from 1 to 12, preferably 1 to 8;

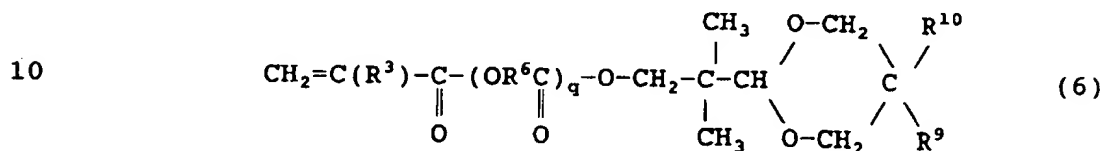


wherein R^3 has the same meaning as defined for formula (3), R^6 is an alkylene group having 2 to 8, preferably 2 to 5, carbon atoms; R^7 is a tetrahydrofuryl group, and p is

35 an integer from 1 to 8, preferably 1 to 4;



wherein R^3 , R^6 , and p have the same meanings as defined above, R^8 is a phenyl group, optionally substituted with
 5 an alkyl group having 1 to 12, preferably 1 to 9, carbon atoms; and



wherein R^3 and R^6 have the above defined meaning and q is
 15 an integer from 0 to 8; and R^9 and R^{10} are individually a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms, a group $-\text{R}^{11}-\text{A}$, wherein R^{11} is an alkylene group containing 1 to 6 carbon atoms and A is a (meth)acrylate group.

20 In addition, commercially available products obtained in the trademarks of Aronix M111, M113, M114, M117 (manufactured by Toagosei Chemical Industry Co., Ltd.), KAYARAD TC110S, R629, R644 (manufactured by Nippon Kayaku Co., Ltd.), Viscoat 3700 (manufactured by Osaka
 25 Organic Chemical Industry, Ltd.), and the like can be used.

Among these, phenoxy polyethylene glycol acrylate, acryloyl morpholine, isobornyl acrylate, and dicyclopentanyl acrylate are preferred.

30 Examples of the poly-functional compounds include trimethylolpropane tri(meth)acrylate, tri(meth)acrylate of trimethylolpropane ethylene oxide addition triol, tri(meth)acrylate of trimethylolpropane propylene oxide addition triol, di(trimethylolpropane)
 35 tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, ethylene glycol

di(meth)acrylate, tetra ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, hydroxypivalic acid
5 neopentyl glycol di(meth)acrylate, trimethylolpropane trioxyethyl (meth)acrylate, tris(2-hydroxyethyl)-isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)-isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, di(meth)acrylate of ethylene oxide
10 addition diol of bisphenol A, di(meth)acrylate of propylene oxide addition diol of bisphenol A, and (meth)acrylic acid addition compounds of bisphenol A diglycidyl ether polymer.

In addition, Yupimer UV, SA1002, SA2007
15 (manufactured by Mitsubishi Chemical Co., Ltd.), Viscoat 700 (manufactured by Osaka Organic Chemical Industry, Ltd.), KAYARAD MANDA, DPHA, P-604, DPCA-20, 30, 60, 120, HX-620, D-310, 330 (manufactured by Nippon Kayaku Co., Ltd.), Aronix M-210, 215, 315, 325 (manufactured by
20 Toagosei Chemical Industry Co., Ltd.), and the like are given as commercially available products.

The molecular weight of the monomer possessing at least one (meth)acrylate group is usually from 200 to 3,000 by number average molecular weight.

25 Among the bisphenyl compounds enumerated above, the acrylic acid ester of ethylene oxide addition p-cumylphenol is especially desirable.

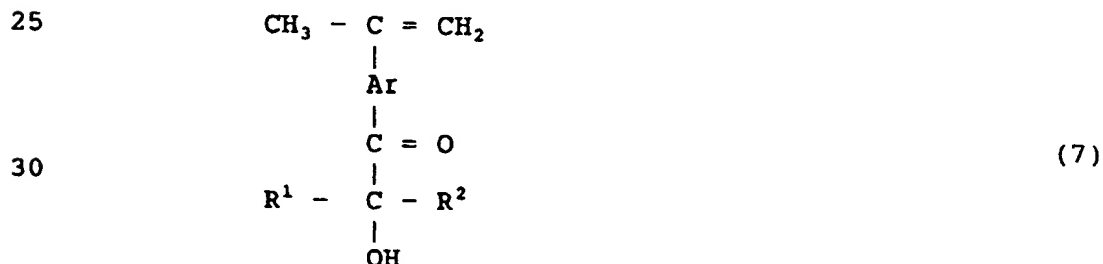
A preferred composition comprises as component (A) 10-80 wt.% of a polymer with a number average
30 molecular weight of 500 or more, and 20-90 wt.% of one or more reactive diluents. The amount of wt% is given in respect to the total composition, unless otherwise stated.

A particularly preferred composition in the event that two or more of the (meth)acrylate
35 group-containing compounds are used in combination as the

component (A) comprises, 20 to 60 wt% of (I) the polymer with a number average molecular weight or 500 or more, 5 to 40 wt% of (II) of a (meth)acryl-functional reactive diluent not comprising an aromatic ring such as in particular (meth)acrylate morpholine, and 10 to 50 wt% of (III) a monomer possessing at least one aromatic ring in a molecule.

Given as examples of the monomer possessing at least one aromatic ring in a molecule (III) are benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, phenoxy polyethylene glycol (meth)acrylate, 2-(meth)acrylate oxyethyl phthalic acid, 2-(meth)acrylateoxyethylhexahydro phthalic acid, 2-(meth)acryloxypropyl phthalic acid, 2-(meth)acrylateoxypropyltetrahydro phthalic acid, 2-(meth)acrylateoxypropylhexahydro phthalic acid, 2-(meth)acrylateoxyethyl succinic acid, the bisphenyl compounds and the compounds represented by the above-mentioned formula (5).

The radiation polymerization initiator having the group represented by above-mentioned formula (1), which is the component(B) in the present invention, can be obtained by the polymerization or oligomerization of the compound of the following formula (7),



wherein R^1 and R^2 are the same as defined in the formula (1).

As the alkyl group containing 1 to 5 carbon atoms represented by R^1 or R^2 , methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, t-butyl group, n-pentyl group, and i-pentyl group are given as
5 specific examples. Of these, particularly preferred are the alkyl groups having 1 to 3 carbon atoms. The symbol n in the formula (1) may be varied depending on the polymerization degrees of the compound (7). It is desirable that the value be 2 to 50, particularly 2 to 20.

10 Particularly preferred compounds used as the radiation polymerization initiator (B), are those with a methyl group for R^1 and R^2 , wherein n is a number of 2 to 50. ESACURE KIP150 (manufactured by Lamberti Co.) can be used as a commercially available product.

15 The number average molecular weight of the compound B generally is between 300-9000, preferably between 400 and 4000.

The number average molecular weight is measured with GPC using a standard method.

20 It is desirable that the radiation polymerization initiator of the component (B) is incorporated in the composition of the present invention in an amount of 0.1 to 10 wt%, preferably 1 to 10 wt%.

If this amount is less than 0.1 wt%, the curing
25 rate is sometimes retarded; if more than 10 wt%, the storage stability of the composition and the properties of the cured products may be impaired.

Given as examples of other radiation
polymerization initiators which may be used together with
30 the above-mentioned radiation polymerization initiators (B) in composition of the present invention are
1-hydroxycyclohexylphenyl ketone, 2,2-dimethoxy-
2-phenylacetophenone, monoacylphosphine, xanthone,
fluorenone, benzaldehyde, fluorene, anthraquinone,
35 triphenylamine, carbazole, 3-methylacetophenone,

4-chlorobenzophenone, 4,4'-dimethoxybenzophenone,
4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl
ether, benzoin ethyl ether, benzyl methyl ketal,
1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one,
5 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone,
diethylthioxanthone, 2-isopropylthioxanthone,
2-chlorothioxanthone, 2-methyl-1-
[4-(methylthio)phenyl]-2-morpholinopropan-1-one,
2,4,6-trimethylbenzoyl diphenylphosphine oxide, and
10 bisacylphosphine oxide.

As examples of commercially available products,
Irgacure 184, 651, 500, 907, 369, CG24-61 (manufactured by
Ciba Geigy), Lucirin TPO (manufactured by BASF), Darocure
1116, 1173 (manufactured by Merck Co.), and Uvecryl P36
15 (manufactured by UCB) can be given.

When these other radiation polymerization
initiators are used, a desirable proportion is in the
range of 0.1 to 10 wt% in the composition of the present
invention, but preferably, the amount is less than 3 wt%,
20 in particular less than 1 wt%.

The composition of the present invention may
comprize at least one polymerizable non-acrylate, non-
methacrylate monomer as a component (C) for the purpose of
adjusting the viscosity or curability of the composition,
25 or the dynamic properties of the cured products.

A vinyl group-containing compound, such as
N-vinyl pyrrolidone, N-vinyl formamide or N-vinyl
caprolactam, is preferably used as such a polymerizable
monomer.

30 It is desirable that such a component (C) is
incorporated in an amount of less than 50 wt%, for example
1-50 wt%, preferably 5 to 30 wt%, in the composition of
the present invention.

In addition to the above-described components,
35 additives can be added to the composition of the present

invention as required and in conventional amounts.

As examples of the additives which can be added, photosensitizers, antioxidants, photostabilizers, silane coupling agents, aging preventives, thermal polymerization
5 inhibitors, leveling agents, surfactants, coloring agents, UV absorbers, preservatives, plasticizers, lubricants, solvents, fillers, wettability improvers, and coating surface improvers are given.

Examples of the photosensitizers include
10 triethylamine, diethylamine, N-methyldiethanoleamine, ethanolamine, 4-dimethylaminobenzoic acid, 4-methyldimethylaminobenzoate, 4-ethyl dimethylaminobenzoate, 4-isoamyldimethylaminobenzoate, and commercially available
15 products such as Uvecryl P102, 103, 104, 105 (manufactured by UCB), and the like.

Commercially available antioxidants include Irganox 1010, 1035, 1076, 1222 (manufactured by Ciba Geigy); of the UV absorbers, Tinuvin P 234, 320, 326, 327,
20 328, 213 (manufactured by Ciba Geigy), Sumisorb 110, 130, 140, 220, 250, 300, 320, 340, 350, 400 (manufactured by Sumitomo Chemical Industries Co., Ltd.); and of the photostabilizers, Tinuvin 292, 144, 622LD (manufactured by Ciba Geigy), Sanol LS-770, 765, 292, 2626, 1114, 744
25 (manufactured by Sankyo Chemical Co.). Examples of the silane coupling agents include γ -aminopropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -acryloxypropyltrimethoxysilane, and commercially available products such as SH6062, SZ6030 (manufactured by
30 Toray-Dow Corning Silicone Co.), and KBE903, KBM803 (manufactured by Shin-Etsu Silicone Co., Ltd.). Antigene W, S, P, 3C, 6C, RD-G, FR, AW (manufactured by Sumitomo Chemical Industries Co., Ltd.) and the like are given as commercially available products of the aging preventives.

35 Beside the above-described components, other

polymers or oligomers may be incorporated as other additives to the composition of the present invention. Such polymers or oligomers include, for example, epoxy resin, polyamide, polyamideimide, polyurethane, 5 polybutadiene, chloroprene, polyether, polyester, pentadiene derivatives, styrene/butadiene/styrene block copolymer, styrene/ethylene/butene/styrene block copolymer, styrene/isoprene/styrene block copolymer, petroleum resin, xylene resin, ketone resin, 10 fluorine-containing oligomer, silicon-containing oligomer, and polysulfide oligomer.

The radiation curable resin composition for molding by polymerization in dies of the present invention can be prepared by mixing the above-mentioned components 15 by a conventional means.

The viscosity of the composition of the present invention thus prepared may be adjusted in the range usually of 100 to 20,000 cps/25°C, and preferably of 500 to 10,000 cps/25°C.

20 The composition of the present invention is cured by a radiation. The radiation here includes radiations such as, for example, infrared light, visible light, ultraviolet light, X-rays, electron beams, α -rays, β -rays, and γ -rays. Ultraviolet light is preferred among 25 these.

EXAMPLES

The present invention will be hereinafter described in more detail by way of examples which are 30 given for illustration of the present invention and shall not to be construed as limiting the present invention. In the examples below, part(s) by weight is simply referred to as part(s).

35 Preparation of a resin composition

50 parts of an acrylic acid addition compound of bisphenol A diglycidyl ether polymer (Ripoxy VR-77, manufactured by Showa Highpolymer Co., Ltd.), 30 parts of acrylic acid ester of ethylene oxide addition

5 p-cumylphenol (Aronix M110, manufactured by Toagosei Chemical Industry Co., Ltd.), 10 parts phenoxy diethylene glycol acrylate (Viscoat 192, manufactured by Osaka Organic Chemical Industry, Ltd.), and 10 parts of acryloyl morpholine (ACMO. manufactured by Teijin Co., Ltd.) were

10 placed in a reaction vessel equipped with a stirrer, and the mixture was stirred at 50 to 60°C to obtain a resin composition.

Example 1

15 100 parts of the above resin composition and 5 parts of a radiation polymerization initiator, which is an oligomer of 2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propan-1-one with a molecular weight distribution from 408 to about 2,000 (ESACURE

20 KIP150, manufactured by Lamberti Co.), were placed in a reaction vessel equipped with a stirrer. The mixture was stirred at 50 to 60°C to obtain a composition of the present invention.

Example 2

25 A composition of the present invention was prepared in the same manner as in Example 1, except that 5 parts of a radiation polymerization initiator, which is a mixture of 70 wt% of oligo-2-hydroxy-2-methyl-1-[4-(1-methylvinyl)-phenyl]propan-1-one with a molecular

30 weight distribution from 408 to about 2,000 and 30 wt% of 2-hydroxy-2-methyl-1-phenylpropan-1-one (ESACURE KIP100F, manufactured by Lamberti Co.) was used as a radiation polymerization initiator.

Comparative Example A

A comparative composition was prepared in the same manner as in Example 1 using 3 parts of 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (Lucirin TPO, manufactured by BASF) as a radiation polymerization initiator.

Comparative Example B

A comparative composition was prepared in the same manner as in Example 1 using 3 parts of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (Irgacure 907, manufactured by Ciba Geigy) as a radiation polymerization initiator.

Comparative Example C

A comparative composition was prepared in the same manner as in Example 1 using 5 parts of 2-hydroxy-2-methyl-1-phenylpropanone (Darocure 1173, manufactured by Merck Co.) as a radiation polymerization initiator.

Test Example

The compositions prepared in the Examples and Comparative Examples were evaluated as follows:

(1) Evaluation of transparency

The composition was charged into a space between two sheets of glasses with a thickness of 1 mm. The thickness of the composition between the glasses was adjusted to 1100 μm using spacers. UV light was irradiated from the both side at a dose of 0.5 J/cm² each side. The slide glasses were removed to obtain a sheet of cured composition to be used for the transparency evaluation test. Another sheet of cured composition with a thickness of 100 μm , to be used as a control, was prepared in the

same manner. The transmittance 400, 500, and 600 nm of the sheet with a 1100 μm was measured at using an absorptiometer.

5 (2) Evaluation of resistance to coloration upon exposure to light

1. Preparation of test specimens

 A cured test specimen with a thickness of 100 μm was prepared by applying the composition to a glass sheet using a 250 μm applicator, followed by irradiation of UV light at a dose of 1.0 J/cm². The test specimen was subjected to a UV light exposure test for 7 days using a photoresistant tester (QUV, manufactured by Q-Panel Co.).

2. Measurement of color difference

15 The color difference was measured using a color differentiator (E80*, manufactured by Nippon Denshoku Co., Ltd.) using a C-light source and reflection from an angle of 45°. The color difference (ΔE) before and after exposure to UV light was determined.

20

(3) Evaluation of dimensional stability

 The composition was applied to a PET film with a thickness of 120 μm using a 130 μm applicator, followed by irradiation of UV light at a dose of 0.5 J/cm². The PET film was cut into 7 cm squares and allowed to cool for 30 minutes, followed by storing for 2 hours at 60°C. The test specimens were allowed to cool for 30 minutes and the warpage at the four corners was measured by a caliper and the average of the four corners was determined.

30 The results of evaluations on the transparency, the resistance to coloration upon exposure to light, and the dimensional stability are shown in Table 1.

TABLE 1

		Example		Comparative Example		
		1	2	A	B	C
5	Transparency Transmittance (%)					
	400 nm	85	85	0	79	85
	500 nm	99	98	90	92	99
	600 nm	100	99	98	92	100
	Color Difference (ΔE)	5	5	11	15	4
10	Dimensional stability					
	Warping (mm)	15	17	16	19	23

15 The radiation curable resin composition of the present invention preferably exhibits (after being cured) a color difference (ΔE) after exposure to UV light for 7 days (if tested as described above) of less than 9; the dimensional stability measured as warping is preferably less than 20 mm. The color difference (ΔE) is preferably less than 7; the warping preferably is less than 18 mm.

20 The radiation curable resin composition of the present invention preferably exhibits (after being cured) a transparency of more than about 82% transmittance at 400, 500 and 600 nm, if tested as described above.

25 The radiation curable resin composition of the present invention exhibits a high curing rate and produces molded products with a high transparency, excellent resistance to coloration upon exposure to light, and superior dimensional precision. This radiation curable resin composition is very useful as a material for optical

30

parts which are molded while the resins are being polymerized in dies, such as lenses, optical disks, prisms, and lens sheets.

WHAT IS CLAIMED IS:

1. A radiation curable composition for molding by
 5 polymerization in dies comprising,
 (A) at least one compound having at least one
 (meth)acrylate group and
 (B) at least one photopolymerization initiator being
 an oligomer having a molecular weight of about
 10 300 to about 9000 and comprising on average more
 than 1.5 (α -ketone, β -hydroxydialkylethylbenzyl
 groups.
 2. Composition according to claim 1, wherein the
 photoinitiator has a group represented by the
 15 following formula (1),



wherein R^1 and R^2 are alkyl groups having 1 to 5
 30 carbon atoms and n is a recurring number of the group
 (1).

3. Composition according to any one of claims 1-2,
 wherein n is 2 to 50.
4. Composition according to any one of claims 1-3,
 35 wherein the photopolymerization initiator is present
 in an amount of about 0.1 to about 10 wt.% relative
 to the total composition.

5. Composition according to any one of claims 1-4, wherein the composition comprises at least one photopolymerisation initiator other than component B.
6. Composition according to any one of claims 1-5, wherein component (A) comprises a polymer, a monomer or a mixture thereof.
7. Composition according to any one of claims 1-6, wherein the composition comprises an oligomer having at least one (meth)acrylate group with a number average molecular weight of 300-20,000.
8. Composition according to any one of claims 1-7, wherein the composition comprises a monomer having at least one (meth)acrylate group and having one or more aromatic rings.
9. Composition according to any one of claims 1-8, wherein the composition comprises as the component (A) 10-80 wt.% of a polymer with a number average molecular weight of 500 or more and 20-90 wt.% of one or more reactive diluents.
10. Composition according to claim 9, wherein the composition comprises as the component (A)
 - A1 20-60 wt.% of a polymer with a number average molecular weight of 500 or more,
 - A2 5-40 wt.% of a (meth)acryl functional reactive diluent not comprising an aromatic group,
 - A3 10-50 wt.% of at least one monomer having least one aromatic ring in the molecule.
11. Composition according to claim 10, wherein component A2 is (meth)acryloylmorpholine.
12. Composition according to any one of claims 1-11, wherein the composition further comprises as a component (C) at least one vinyl group containing compound in an amount of 1 to 50 wt.%.

13. Composition according to any one of claims 1-12, wherein the composition has a viscosity of 100-20,000 cps at 25°C.
- 5 14. Molded product obtained by polymerization of a composition according to any one of claims 1-13, in a die.
- 15 15. Product according to any claim 14, wherein the product is a lens, optical disk, prism or lens sheet.
- 10 16. Product according to any one of claims 14-15, wherein the transparency of the product at 1100 μm thickness is more than about 82% transmittance at 400, 500 and 600 nm, using a 100 μm thick sheet as a reference.
- 15 17. Product according to any one of claims 14-16, wherein the product has a color difference (ΔE) after exposure to UV light for 7 days of less than about 9.
18. Product according to any one of claims 14-17, wherein the product has a dimensional stability measured as warping of less than 20 mm.
- 20 19. Molded product obtained by polymerization of a radiation curable composition comprising a compound having at least one (meth)acrylate functional group and at least one photopolymerization initiator, in a die, wherein the transparency of the product at 1100 μm thickness is more than about 82% transmittance at 400, 500 and 600 nm, using a 100 μm thick sheet as a reference and a color difference (ΔE) after exposure to UV light for 7 days or less than about 9.
- 25 20. Molded product according to claim 19, wherein the product has a dimensional stability measured as warping of less than 20 mm.
- 30 21. Molded product according to any one of claims 19-20, wherein the product is a lens, optical disk, prism or lens sheet.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/NL 97/00387

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F2/50 G03F7/031

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 161 463 A (F. LLI LAMBERTI S.P.A.) 21 November 1985 see page 6, line 29 - page 7, line 15; claims 1,5	1-21
X	EP 0 341 560 A (MERCK PATENT GMBH.) 15 November 1989 see claim 1	1-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

13 October 1997

Date of mailing of the international search report

28.10.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cauwenberg, C

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/NL 97/00387

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 161463 A	21-11-85	BR 8501709 A	10-12-85
		CA 1323463 A	19-10-93
		JP 1617436 C	12-09-91
		JP 2036582 B	17-08-90
		JP 60252443 A	13-12-85
		JP 2160803 A	20-06-90
		JP 7080927 B	30-08-95
		US 4672079 A	09-06-87

EP 341560 A	15-11-89	DE 3816304 A	23-11-89
		AU 627177 B	20-08-92
		AU 3472489 A	16-11-89
		CA 1336091 A	27-06-95
		DE 58907593 D	09-06-94
		JP 1319504 A	25-12-89
